High Sensitivity of Electron Transfer Rates within Nafion Coatings Saturated with $Os(bpy)_3^{2+}$ to the Extent of Hydration of the Coating

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ABSTRACT

The sensitivity of the electrochemical responses obtained from electroactive counterions incorporated in Nafion coatings to the extent of hydration of the coatings[27-38] is shown to be enhanced significantly when the electroactive ion is the only counterion present in the coating. Nafion coatings fully saturated with $Os(bpy)_3^{2+}$ exhibit unusually narrow and sharply peaked anodic currents in first-scan oxidative voltammograms. This voltammetric feature is accompanied by the expulsion of one-third of the Os complex from the coating. The counterion actually ejected is primarily $Os(bpy)_3^{3+}$. As the $Os(bpy)_3^{3+}$ counterions are ejected, H_2O molecules enter the coatings. The quantity of H_2O molecules incorporated is so large that the mass of the coating (monitored with a quartz crystal microbalance) increases despite the ejection of the heavy $Os(bpy)_3^{3+}$ cations. After several voltammetric cycles, normally shaped voltammograms are obtained that are relatively insensitive to the initial state of hydration of the coatings. The contrasting behaviors of hydrated and unhydrated coatings are compared, and possible explanations are offered for the differences observed.

Nafion deposited on electrode surfaces is one of the most extensively investigated polyelectrolyte coatings that have been employed to modify the behavior of electrodes. The facile incorporation and retention by Nafion coatings of cationic complexes with hydrophobic ligands such as 2,2′-bipyridine have induced many previous workers to examine the electrochemical responses of electroactive complexes of this type within Nafion coatings. Representative early examples can be found in Ref. 1-13. Most previous studies have involved coatings in which only a portion of the initially present, electroinactive counterions (*e.g.*, H^+, Na^+) were replaced by electroactive ions, but in one case experiments were conducted with Nafion coatings that had been exposed to solutions of $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) for extended periods so that $Os(bpy)_3^{2+}$ cations became the only counterions within the coating.[14] Electro-oxidation of these counterions to $Os(bpy)_3^{3+}$ required that some of them be ejected from the permselective, polyanionic Nafion to maintain electroneutrality within the coating. Such ejection was monitored by means of microprobe electrodes positioned just above the coatings, but only qualitative measurements were possible because of variability in the sensitivity of the microprobe electrodes at Nafion coated electrodes.[14] The present study constitutes an extension and elaboration of this previous work. The use of rotating ring-disk electrodes to monitor the ejection of counterions from Nafion coatings allowed quantitative determinations to be obtained. In addition, we observed a high sensitivity of the voltammetric responses obtained from coatings saturated with $Os(bpy)_3^{2+}$ to the water content of the coatings. Procedures for varying the extent of hydration during the preparation of coatings were developed to demonstrate the dramatically different types of behavior that can be encountered. Finally, a quartz crystal microbalance (QCM) was employed to monitor the changes in the mass of coatings that accompanied the ejection of counterions. The somewhat surprising result of these measurements was that the oxidative ejection of $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{2+}$ cations from coatings saturated with $Os(bpy)_3^{2+}$ was accompanied by an increase instead of a decrease in the mass of the coating.

While this study was in progress we received a preprint of a related study by Shin *et al.*[15] In those instances where similar experiments were conducted in the two studies, the results are in reasonable agreement. A recent report by Tjärnhage and Sharp also describes the application of QCM measurements to Nafion-$Os(bpy)_3^{3+/2+}$ coatings but at loading levels below full saturation.[16]

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Experimental

Materials.—$Os(bpy)_3Cl_2 \cdot 6H_2O$ (bpy = 2,2′-bipyridine) was prepared by a conventional procedure.[17] Nafion (equivalent weight = 1100) was obtained from Aldrich Chem. Co. as a 5 weight percent (w/o) solution in a solvent consisting of a mixture of aliphatic alcohols and water. More dilute stock solutions with concentrations of 0.5 or 2.5 w/o were prepared by diluting the commercial sample with isopropanol. Other chemicals were reagent grade and were used as received. Glassy carbon disk electrodes (Tokai Carbon Co.) with an area of 0.2 cm^2 were mounted on stainless steel shafts with heat-shrinkable tubing. The rotating glassy carbon ring-glassy carbon disk electrode was from Pine Instrument Co.; dimensions: disk radius = 0.280 cm; inner ring radius = 0.312 cm; ring width = 0.084 cm. Its calculated collection efficiency[18] was 0.37, which matched that measured with the $Fe(CN)_6^{3-/4-}$ couple.

Apparatus and procedures.—Most experiments were carried out with conventional electrochemical cells and a home-built, computer-controlled, bipotentiostat and data acquisition system. Chronocoulometric experiments were conducted with a BAS-100A instrument from Bioanalytical Systems, Inc. The thickness of coatings was estimated with a profilometer (Dektak Model 3030) using the smallest available stylus force (0.01 mN). The electrochemical quartz crystal microbalance measurements were conducted with a home-built circuit and cell modeled after those described by Baker and Reynolds.[19] The instrument was operated with a nominal crystal oscillation frequency of 10 MHz. Actual frequencies were determined with a Phillips Model PM6654C high-resolution frequency counter with a precision of ±1 Hz. Gold-coated quartz crystals were obtained from the International Crystal Manufacturing Co. Nafion coatings were applied to the crystals by spin-coating from 2.5 w/o solutions. The instrument was calibrated by depositing Ag on the bare gold electrodes at constant current and measuring the slope of the resulting frequency-time curves.

Nafion coatings were applied to glassy carbon disk electrodes that had been polished with 0.5 μm alumina and sonicated in pure water for 5 min. A spin-coating procedure was utilized when possible: 15 μl of a 5 w/o solution of Nafion were spread across the electrode surface, and the electrode was rotated at 3000 rpm for 30 s. Profilometric measurements indicated that the resulting coatings had reasonably uniform thicknesses of *ca.* 250 ± 16 nm. To coat the disk but not the ring of the ring-disk electrode required care and practice: 4 μl of a 0.5 w/o Nafion stock solution were transferred to the disk and carefully spread across its

entire surface by manipulation with the tip of the micropipette. The solvent was then allowed to evaporate at room temperature.

Different pretreatment procedures were employed to obtain coatings that exhibited two limiting properties. Hydrated coatings: the stock solution from which the coatings were cast was evaporated at room temperature in an atmosphere controlled to maintain the relative humidity in the range between 45 and 60%. The drying time varied but never exceeded 30 min. The resulting coating was soaked in water for 10 min before transfer to a 1 m*M* $Os(bpy)_3^{2+}$ solution for loading which was typically complete within 2 h. Unhydrated coatings: the procedure described above for hydrated coatings was employed except that the intermediate step in which the freshly deposited coating was soaked in water was omitted. The freshly cast coating was transferred directly to the 1 m*M* $Os(bpy)_3^{2+}$ loading solution. Periods of 24 to 48 h were typically required to obtain full loading.

The supporting electrolyte for all electrochemical measurements was 0.1 *M* CH_3COOLi – 0.1 *M* CH_3COOH. Potentials were measured and are quoted with respect to an Ag/AgCl (KCl sat) reference electrode which had a potential of 0.20 V *vs.* normal hydrogen electrode (NHE). Experiments were carried out at the ambient laboratory temperature, 23 ± 1°C.

Results

Shapes of cyclic voltammograms for Nafion coatings saturated with $Os(bpy)_3^{2+}$.—Only a few previous reports have dealt with the behavior of Nafion coatings in which all the protons or alkali cations initially present as counterions in the polyanionic Nafion were replaced by electroactive cations.[14,15] The behavior of such fully loaded coatings is especially interesting when the incorporated ions are electro-oxidizable so that the positive charge of each counterion is increased. In such cases cations must be ejected from the coating (or anions incorporated) to maintain electroneutrality. Such cation ejection from Nafion coatings that had been fully loaded with $Os(bpy)_3^{2+}$ counterions was described in a previous report from this laboratory.[14] The shapes of cyclic voltammograms with such coatings during the first scan of the electrode potential toward more positive values are dramatically different from all subsequent scans for reasons that are associated with the cation ejection.[14] However, we have now found that the detailed shapes of the initial voltammetric responses are highly dependent on the procedures employed in preparing the Nafion coatings as well as the extent of their loading with $Os(bpy)_3^{2+}$. For example, the voltammograms shown in Fig. 1A and B were recorded with nominally similar coatings that had been pretreated somewhat differently before they were fully loaded with $Os(bpy)_3^{2+}$. The sharp anodic spike in the first-scan, current-potential curve in Fig. 1A resembles the one reported in our previous study.[14] However, a contrasting, broader anodic peak at a less positive potential (Fig. 1B) was obtained when the Nafion coating was prepared by a slightly different procedure: the coating used to obtain Fig. 1A was applied to the electrode by spin-coating and then treated according to the unhydrated coating procedure described in the Experimental section. The coating was immersed in a 1 m*M* solution of $Os(bpy)_3^{2+}$ for 24 h to obtain full loading, *i.e.*, to incorporate one $Os(bpy)_3^{2+}$ cation for every two SO_3^- groups of the Nafion. (A coating was assumed to be fully loaded with $Os(bpy)_3^{2+}$ when the coulometric area defined by the first oxidative scan, during which all the $Os(bpy)_3^{2+}$ was oxidized to $Os(bpy)_3^{3+}$, was 50% larger than the corresponding area in the steady-state voltammogram.) The electrode with the fully loaded coating was washed with water and transferred to a pure supporting electrolyte solution to record the voltammograms shown in Fig. 1A. The solid curve was the response obtained during the first cycling of the potential between 0.2 and 1.0 V. The dotted curve shows the steady-state response obtained after three or more cycles. This voltammogram was stable to further cycling. The sharply spiked shape of the first-scan voltammogram was reasonably reproducible as long as the humidity of the atmosphere in which the freshly cast Nafion coating was allowed to dry was controlled. Coatings dried at humidity levels below *ca.* 40% produced first-scan voltammograms with more erratic shapes.

The voltammograms in Fig. 1B were obtained with a hydrated coating that was prepared in the same way as that in Fig. 1A except that the freshly cast coating was soaked in water for 10 min before it was loaded with $Os(bpy)_3^{2+}$. The first potential scan to more positive potentials with the fully loaded coating resulted in a rounded instead of a spiked anodic peak at a significantly less positive potential (solid curve in Fig. 1B). However, the steady-state voltammogram obtained after several cycles of the potential was essentially the same as that obtained with the unhydrated coating (dotted curves in Fig. 1A and B).

The first-scan voltammograms shown in Fig. 1A and B represent the limiting cases of unhydrated and hydrated coatings. Responses with shapes intermediate between the two limiting cases resulted when modified procedures were used in the preparation of coatings. The first-scan responses for unhydrated coatings were sensitive not only to the humidity of the atmosphere in which the casting solvent was evaporated, but also to the quantity of water in the original, largely alcoholic casting solvent, and the con-

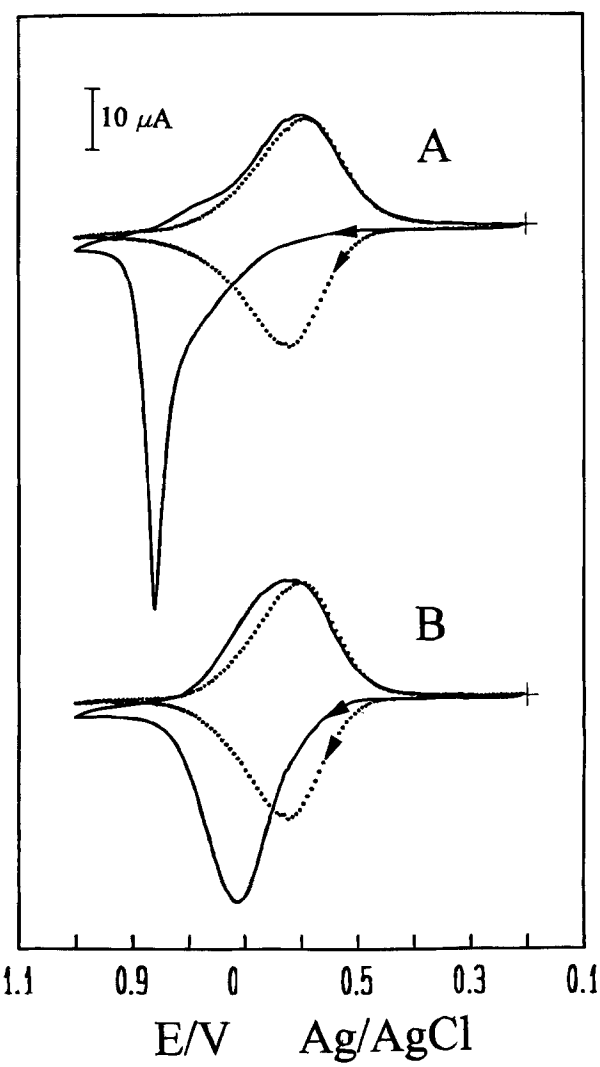

Fig. 1. Comparison of cyclic voltammograms recorded with Nafion coatings prepared in (A) unhydrated and (B) hydrated states (see Experimental) and fully loaded with $Os(bpy)_3^{2+}$. Initial potential: 0.2 V. Scan rate: 11.6 mV s^{-1}. Supporting electrolyte: 0.1 *M* CH_3COOLi – 0.1 *M* CH_3COOH. The solid curves show the first scan; the dotted curves are the steady-state responses that resulted after three or four cycles.

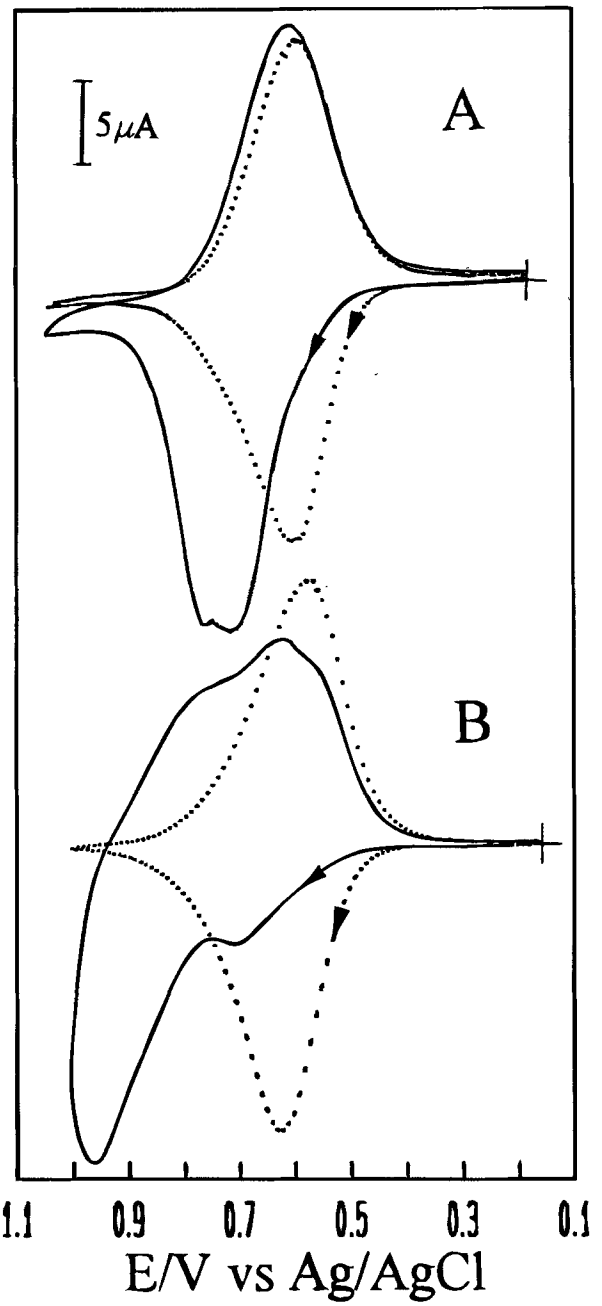

Fig. 2. Variation in voltammetric responses with the procedures employed in preparing Nafion coatings. (A) Freshly cast coating dried at ~25% humidity for 30 min, soaked in water for 10 min, and then loaded with $Os(bpy)_3^{2+}$ from a 1 m*M* solution for 2 h. (B) Freshly cast coating dried in a vacuum oven at 50°C for 24 h before loading with $Os(bpy)_3^{2+}$ from a 1 m*M* solution for 24 h. The solid curves are the first-scan responses; the dotted curves are the steady-state responses obtained after three or four scans. Other conditions as in Fig. 1.

centration of $Os(bpy)_3^{2+}$ in the loading solution. Coatings that were dried for periods in excess of 10 min in an atmosphere with a humidity below ~40% were less susceptible to hydration when soaked for 10 min in pure water as part of the protocol for the preparation of hydrated coatings. For example, the coating used to record the voltammograms in Fig. 2A was dried at 25% humidity. The first-scan voltammogram has a shape that is intermediate between those in Fig. 1A and B. The reason, we believe, is that the coating is partially hydrated. The response shown in Fig. 2B was obtained from a coating that was dried for 20 h at 50°C in a vacuum oven (instead of 10 min at room temperature in air at ~50% humidity) before exposure to the $Os(bpy)_3^{2+}$ loading solution for 24 h. The first-scan voltammogram contains two anodic peaks, the smaller at a potential near that of the single peak in Fig. 1B and the larger at a potential even more positive than the spiked response in Fig. 1A. Despite the longer loading time employed, the area defined by the anodic response in Fig. 2B is smaller than that in Fig. 2A, and both are somewhat less than the value corresponding to full loading. In general, the more aggressive the procedures employed in drying the coatings, the slower their rate of incorporation of $Os(bpy)_3^{2+}$. Hydrated coatings reach saturation loading within 2 h from 1 m*M* solutions of $Os(bpy)_3^{2+}$ while more than 12 h are needed to saturate unhydrated, air-dried coatings.

A noteworthy aspect of all of the responses shown in Fig. 1 and 2 is the similarity of the voltammograms obtained at steady state. Once the quantity of $Os(bpy)_3^{3+/2+}$ present in the coatings is diminished to the point that the ionic current crossing the coating/solution interface is carried entirely by the Li^+ cations of the supporting electrolyte, the cyclic voltammetric response is essentially independent of the procedures or conditions used to prepare the coatings. Similarly, even unhydrated coatings exhibit first-scan voltammograms that match the steady-state response if they are loaded with substantially fewer than one $Os(bpy)_3^{2+}$ cation for every three Nafion sulfonate groups. It is this property that is responsible for the reasonable agreement among previous descriptions of voltammetric responses from Nafion coatings that were prepared by various procedures but not fully loaded with $Os(bpy)_3^{2+}$.

The reproducible response obtained from hydrated coatings (*e.g.*, Fig. 1B) was converted into one resembling that obtained from unhydrated coatings by prolonged exposure of the former to the $Os(bpy)_3^{2+}$ loading solution. In Fig. 3 are shown the responses obtained from three coatings. The first voltammogram (curve 1) was obtained with a hydrated coating that was loaded with $Os(bpy)_3^{2+}$ for 2 h. The re-

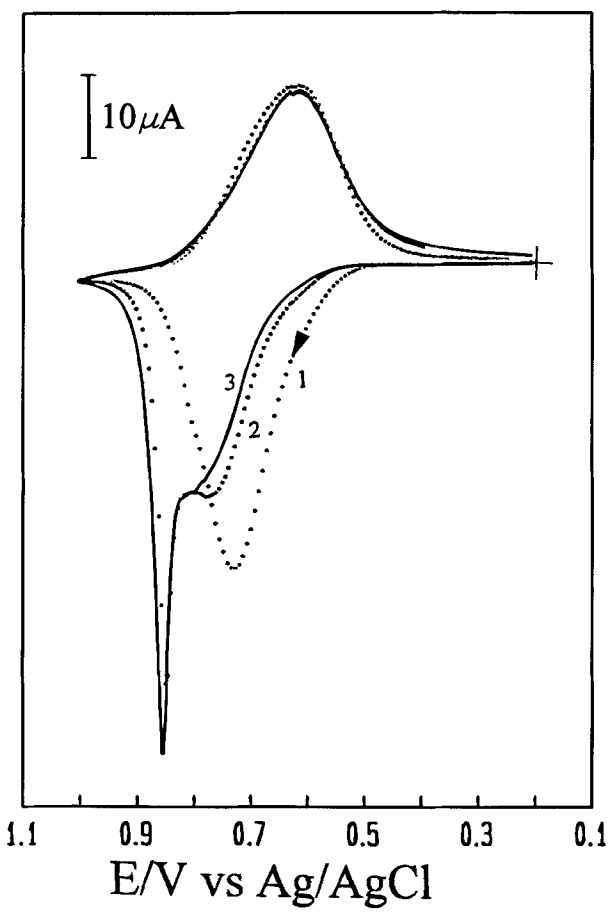

Fig. 3. Effect of prolonged exposure to $Os(bpy)_3^{2+}$ on the voltammetric response of an initially hydrated coating. All three voltammograms were obtained during the first oxidative scan after a hydrated coating was exposed to a 1 m*M* $Os(bpy)_3^{2+}$ solution for (1) 2 h; (2) 1 week; (3) 2 weeks. Other conditions as in Fig. 1.

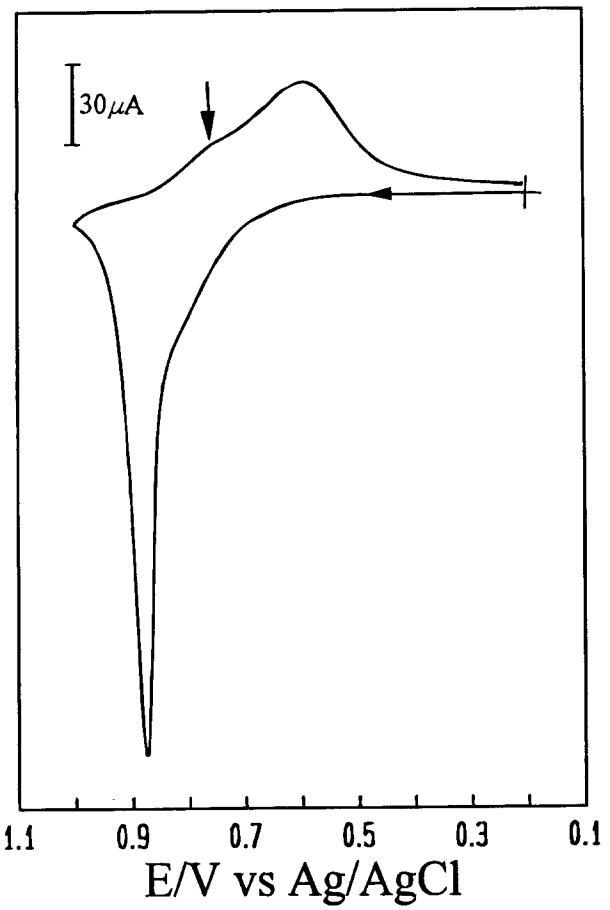

Fig. 4. First-scan cyclic voltammogram for an unhydrated, fully loaded coating on a glassy carbon disk electrode rotated at 9000 rpm. The arrow marks the first cathodic peak. Scan rate = 46.5 mV s^{-1}. Other conditions as in Fig. 1.

sponse resembles that in Fig. 1B. Curves 2 and 3 in Fig. 3 were obtained after the hydrated coatings were exposed to the 1 m*M* $Os(bpy)_3^{2+}$ loading solution for 1 and 2 weeks, respectively. Curve 3 (solid curve) resembles the voltammogram in Fig. 1A showing that prolonged exposure to $Os(bpy)_3^{2+}$ solutions converts an initially hydrated coating into one with properties similar to unhydrated coatings.

Unhydrated, fully loaded coatings that exhibit the anodic spikes at positive potentials in the first oxidative voltammetric scan also typically contain two waves in the first reductive scan (Fig. 1A). The main cathodic peak appears at or near the potential corresponding to the steady-state response, but a smaller cathodic wave reproducibly appears at more positive potentials, not far from that of the sharp anodic spike. A small, cathodic wave at more positive potentials than the prominent cathodic peak was also noted in our previous study[14] and was suggested to arise from partial reincorporation of $Os(bpy)_3^{2+}$ into the Nafion as the $Os(bpy)_3^{3+}$ that had been ejected during the oxidative scan was reduced at the coating/solution interface. This suggestion was examined more critically here by employing a rotating disk electrode in the cyclic voltammetric experiments. The small cathodic wave was just as prominent when the coated electrode was rotated at 9000 rpm (Fig. 4). Since rotation of the electrode rapidly removes any ejected $Os(bpy)_3^{3+}$ cations from the coating/solution interface, the persistence of the small cathodic wave at rotated electrodes shows that it cannot be the result of reincorporation of $Os(bpy)_3^{2+}$ during the first reductive scan of the cyclic voltammogram.

An alternative possibility is that electroneutrality within the fully loaded coatings during the first oxidative scan is maintained not only by ejection of $Os(bpy)_3^{3+}$ cations from the coating (*vide infra*) but also by incorporation of acetate anions into the coating. The resulting $Os(bpy)_3^{3+}$-acetate ion pairs, contained within the Nafion, are not influenced by rotation of the electrode and may be the source of the small cathodic wave during the first reduction cycle. The more positive potential of the small cathodic wave may then be ascribed to the additional driving force favoring the reduction of the ion paired $Os(bpy)^{3+}$ because of the ejection of acetate anions from the polyanionic coatings that accompanies the reduction. This interpretation requires that the normal high cation permselectivity of Nafion coatings be compromised when the coatings are fully loaded with $Os(bpy)_3^{2+}$. To test their permselectivity, Nafion coatings were cast on gold minigrids that subsequently were used to separate two solutions of NaCl with chloride activities that differed by an order of magnitude. Similar experiments were described in a previous report.[20] The potential difference between two reference electrodes immersed in the Nafion-separated solutions of NaCl was measured before and after the Nafion coating had been fully loaded with $Os(bpy)_3^{2+}$. The results, summarized in Table I, show that the cation permselectivity of the unhydrated Nafion is diminished by loading to saturation with $Os(bpy)_3^{2+}$. The previous report[20] showed that high cation permselectivity is retained by Nafion coatings in which less than saturation amounts of $Os(bpy)_3^{2+}$ are incorporated. The data in Table I indicate that unhydrated, fully loaded coatings are less permselective. The decrease in ΔE from 52 mV (59 mV corresponds to ideal cation permselectivity) to ~30 mV after full loading with $Os(bpy)_3^{2+}$ indicates that anions are not completely excluded from such coatings, a result which is compatible with the interpretation suggested above for the origin of the second, small cathodic wave in the first reductive scan in voltammograms such as those in Fig. 1A and 4. The fully loaded, hydrated Nafion coating appears to retain its permselectivity after transfer to the NaCl supporting electrolyte solution (Table I) and such hydrated coatings do not exhibit two cathodic peaks in the first scan voltammograms (Fig. 1B).

Effect of pretreatments on coating thickness.—The thicknesses of the spin-coated Nafion coatings were estimated from measurements with a profilometer. The coatings, pretreated by various procedures were scanned with the profilometer immediately after the pretreatment procedure was completed. The results, summarized in Table II, showed that the unhydrated coatings were not significantly thinner than hydrated coatings even when the hydration period was extended. However, fully loading the hydrated or unhydrated coatings with $Os(bpy)_3^{2+}$ produced increases in their thicknesses that were of comparable magnitude (Table II).

Table I. Potential differences across Nafion coatings supported on gold minigrids in a concentration cell.[a]

Experiment no.	ΔE [b] (mV)	Notes
1	52 ± 3	Os-free coating. No pretreatment
2	52 ± 3	Hydrated coating fully loaded with $Os(bpy)_3^{2+}$
3	30 to 40	Unhydrated coating fully loaded with $Os(bpy)_3^{2+}$; ΔE slowly increases from ~30 mV
4 [c]	40 ± 3	ΔE steady

[a] The two cell compartments contained 0.05 and 0.60 *M* NaCl, respectively, with corresponding NaCl activities of 0.04 and 0.4.[52] A 0.2 ml aliquot of the 5 w/o Nafion stock solution was transferred to the gold minigrid, and the alcoholic solvent was allowed to evaporate. The resulting coated minigrid was mounted in place in an H-cell with O-rings. The solutions of NaCl were carefully introduced on both sides of the Nafion coatings after the pretreatment procedure had been completed.

[b] Difference in potential between Ag/AgCl reference electrodes placed in the two compartments of the concentration cell.

[c] Repeat of experiment no. 3 except that both NaCl solutions contained 0.2 m*M* $Os(bpy)_3^{2+}$ to depress the loss of $Os(bpy)_3^{2+}$ from the coating by reverse ion exchange.

Table II. Effect of pretreatment procedures on thicknesses of Nafion coatings on polished glassy carbon.[a]

Experiment no.	Thickness[b] (μm)	Notes
1	0.25 ± 0.02	Unhydrated coating
2	0.26 ± 0.02	Hydrated coating[c]
3	0.27 ± 0.02	After prolonged hydration[d]
4	0.34 ± 0.02	Hydrated; fully loaded[e]
5	0.34 ± 0.02	Unhydrated; fully loaded[f]

[a] All coatings were cast by spin-coating as described in the Experimental section.
[b] Estimated by a profilometric scan across coatings that had the Nafion removed at several points by careful slicing with a fine tipped scalpel. The values listed are averages of the thicknesses measured at three different portions of the coatings.
[c] Hydrated by soaking in water for 1 h.
[d] Hydrated by soaking in water for 12 h.
[e] Coating from experiment no. 3 after full loading with $Os(bpy)_3^{2+}$.
[f] Coating from experiment no. 1 after full loading with $Os(bpy)_3^{2+}$.

Ejection of $Os(bpy)_3^{3+/2+}$ from coatings fully loaded with $Os(bpy)_3^{2+}$.—In a previous report, the ejection of $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{2+}$ cations from Nafion coatings that had been saturated with $Os(bpy)_3^{2+}$ counterions that were subsequently electro-oxidized to $Os(bpy)_3^{3+}$ was detected by means of microelectrode probes placed close to the coating surface.[14] This technique provided good detection sensitivity but was less useful in obtaining quantitative data on the counterion ejection. In the present experiments a rotating glassy carbon ring-disk electrode was employed as in previous studies,[21-23] to monitor the ejection of counterions from Nafion coatings that had been carefully deposited on the disk but not the ring electrode. The coatings on the disk were loaded to saturation with $Os(bpy)_3^{2+}$, washed, and transferred to the pure supporting electrolyte solution where the ring and disk currents were monitored during the first scan of the disk potential to more positive values as the electrode was rotated at 1600 rpm. In Fig. 5A and B are shown the results of two such experiments with a hydrated Nafion coating. In Fig. 5A, the potential of the ring electrode was maintained at 0.2 V, where $Os(bpy)_3^{3+}$ reaching the ring is reduced to $Os(bpy)_3^{2+}$ to produce a cathodic ring current. Only a low background ring current was observed until the disk potential was scanned to values where the oxidation of the $Os(bpy)_3^{2+}$ present in the Nafion coating began near a disk potential of 0.55 V (lower curve in Fig. 5A). As the disk potential was scanned over the anodic peak a large cathodic ring current was observed, demonstrating that substantial quantities of $Os(bpy)_3^{3+}$ were ejected from the coating and transported to the ring. Repetition of the experiment with the potential of the ring electrode at 0.9 V to oxidize $Os(bpy)_3^{2+}$ is shown in Fig. 5B with a freshly loaded Nafion coating on the disk. The quantity of $Os(bpy)_3^{2+}$ ejected from the coating was clearly much smaller than the $Os(bpy)_3^{3+}$ observed in Fig. 5A. Measurements of the areas under the anodic disk current peaks and the two ring current peaks allowed the quantities of $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{2+}$ that were ejected in the two experiments to be calculated from the collection efficiency of the ring-coated disk electrode. Because of the likely effect of the Nafion coating on the collection efficiency, it was measured in separate experiments in which coatings that had been loaded with $Os(bpy)_3^{2+}$ and cycled to obtain the steady-state voltammetric response were used to electro-oxidize $Fe(CN)_6^{4-}$ at the coating/solution interface with the ring electrode potential set at 0 V to reduce the $Fe(CN)_6^{3-}$ that was transported to the ring. The measured collection efficiency was 0.31 compared with the value of 0.37 that was measured when $Fe(CN)_6^{4-}$ was oxidized directly at the uncoated disk. This difference in collection efficiency is probably the result of irregularities in the hydrodynamic flow pattern produced by the presence of the Nafion coating on the disk electrode.

Using the measured value of the collection efficiency with the coated disk electrode, the results of ring-disk experiments like those in Fig. 5A and B were analyzed to compare the measured quantities of $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{2+}$ ejected from the coatings with the quantities calculated on the assumption that electroneutrality within the coatings was maintained entirely by ejection of cations. The results, summarized in the first entry in Table III, indicate that the assumption is verified. Both $Os(bpy)_3^{2+}$ and $Os(bpy)_3^{3+}$ are ejected from hydrated coatings but the latter cation accounts for over 90% of the ejected charge.

The same set of experiments was carried out with unhydrated coatings that produced voltammograms with sharp anodic spikes like the one in Fig. 1A. The results are shown in Fig. 5C and D. The anodic spike in the disk current-potential curve is accompanied by a similarly spiked ejection of $Os(bpy)_3^{3+}$ from the coating (Fig. 5C) but essentially no $Os(bpy)_3^{2+}$ is ejected from the coating (Fig. 5D). The area of the ring current response in Fig. 5C was used to obtain an estimate of the total quantity of $Os(bpy)_3^{3+}$ that was ejected from the coating. The results, summarized in the second entry in Table III, are consistent with the assumption that electroneutrality within the Nafion coating is maintained by the ejection of $Os(bpy)_3^{3+}$. However, the accuracy of the measurements is such that as much as 15% of the balancing charge could have been provided by anion incorporation instead of cation ejection.

Chronoamperometric responses at a rotating ring-disk electrode from coatings fully loaded with $Os(bpy)_3^{2+}$.—The sharply spiked anodic features in voltammograms of unhy-

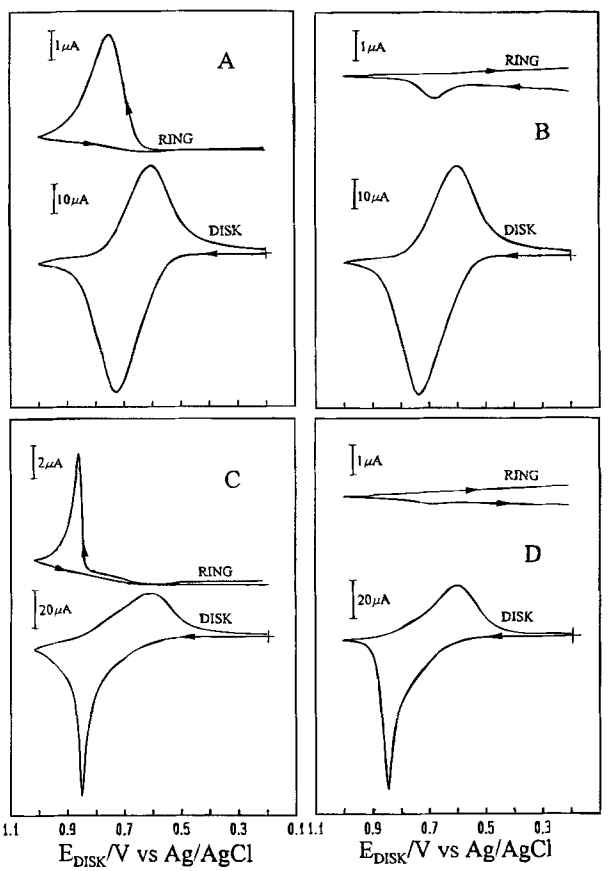

Fig. 5. Use of a rotating ring-disk electrode to measure the quantities of $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{2+}$ ejected from Nafion coatings fully loaded with $Os(bpy)_3^{2+}$ and scanned to potentials where the $Os(bpy)_3^{2+}$ is electro-oxidized to $Os(bpy)_3^{3+}$. The glassy carbon disk electrode was carefully coated with Nafion containing 1.4×10^{-8} mol of SO_3^- groups. The disk electrode potential was scanned at 11.6 mV s^{-1}. Rotation rate: 1600 rpm. Other conditions as in Fig. 1. (A) Hydrated coating, the potential of the glassy carbon ring electrode was 0.2 V; (B) hydrated electrode, the ring potential was 0.9 V; (C) unhydrated electrode, the ring potential was 0.2 V; and (D) unhydrated electrode, the ring potential was 0.9 V.

Table III. Oxidative ejection of $Os(bpy)_3^{3+}$ and $Os(bpy)_3^{2+}$ from Nafion coatings applied to the glassy carbon disk of a rotating ring-disk electrode and fully loaded with $Os(bpy)_3^{2+}$.[a]

	Quantities of counterions ejected[b] (mol)			
	$10^9\Gamma_{Os^{III}}$[c]	$10^9\Gamma_{Os^{II}}$[d]	$10^9(\Gamma_{Os^{III}} + \Gamma_{Os^{II}})$[e]	$10^9(\Gamma_{Os^{III}} + \Gamma_{Os^{II}})_{calc}$[f]
Hydrated electrode	2.0 ± 0.1	0.2 ± 0.1	2.2 ± 0.1	2.1
Unhydrated electrode	2.4 ± 0.3	0	2.4 ± 0.3	2.3

[a] Each coating contained 1.4×10^{-8} mol Nafion sulfonate groups as calculated from $3Q_c/F$ where Q_c is the area in coulombs under the cathodic peaks of steady-state voltammograms (*e.g.*, the dashed curves in Fig. 1) for coatings saturated with $Os(bpy)_3^{3+}$ and F is Faraday's constant.
[b] Evaluated from the areas under the ring current-disk potential curves and the collection efficiency (0.31) of the ring-coated disk electrode.
[c] Quantity of $Os(bpy)_3^{3+}$ ejected; the ring electrode was held at 0.2 V during the scan of the coated disk electrode from 0.2 to 1.0 V.
[d] Quantity $Os(bpy)_3^{2+}$ ejected; the ring electrode was held at 0.9 V.
[e] The sum of $Os(bpy)_3^{2+}$ and $Os(bpy)_3^{3+}$ ejected from the coating.
[f] The calculated quantity of $Os(bpy)_3^{2+}$ and $Os(bpy)_3^{3+}$ ejected to maintain electroneutrality within the coating during the first oxidative scan of the coated electrode assuming no anion incorporation. $(\Gamma_{Os^{III}} + \Gamma_{Os^{II}}) = 0.167\,\Gamma_{SO_3^-}$ where $\Gamma_{SO_3^-}$ is the total quantity of sulfonate groups in the coating and the fraction of 0.167 is the difference between 1/2 and 1/3.

drated, fully loaded coatings (Fig. 1A) have counterparts in the initial current-time curves obtained when the potential of electrodes coated with such coatings is stepped from an initial value where $Os(bpy)_3^{2+}$ is stable, *e.g.*, 0.2 V, to a potential where the oxidation to $Os(bpy)_3^{3+}$ proceeds, *e.g.*, 1.2 V. In Fig. 6, curve 1 shows the unusual current-time curve that is obtained in such an experiment. Several hundred milliseconds elapse after the step-potential is applied to the disk electrode before the anodic current begins to increase significantly. It then passes through a maximum and decreases toward zero. Curve 2 of Fig. 6 shows the current measured simultaneously at the ring electrode with its potential maintained at 0.2 V to detect the $Os(bpy)_3^{3+}$ ejected from the coating on the disk. The cathodic ring current attains its maximum value well after the current at the disk

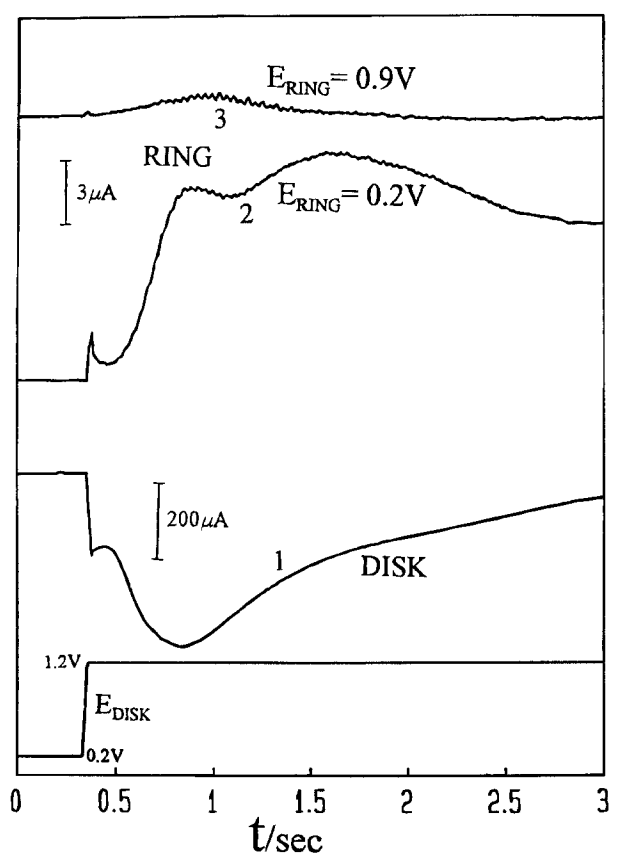

Fig. 6. Chronoamperometric current-time transients obtained with rotated ring-coated disk electrodes. Unhydrated Nafion coatings were carefully applied to the glassy carbon disk electrode and fully loaded with $Os(bpy)_3^{2+}$. The disk potential was stepped from 0.2 to 1.2 V. The ring electrode potentials are shown. The electrode was rotated at 1600 rpm. Other conditions as in Fig. 1.

electrode has passed through its maximum. Since the calculated time required for reactants to cross the insulating gap between the disk and ring electrodes at the rotation rate employed was about 40 ms,[24] the difference in the times at which the disk and ring currents reach their maximum values must reflect a delay in the ejection of $Os(bpy)_3^{3+}$ from the coating on the disk.

When the experiment was repeated with a freshly loaded coating with the ring electrode potential maintained at 0.9 V to detect $Os(bpy)_3^{2+}$, the current response shown in curve 3 of Fig. 6 was obtained. There is a small cathodic response at the ring that is coincident with the application of the potential step and probably results from electronic coupling between the ring and disk control circuits. The absence of a detectable anodic response at the ring electrode indicates that essentially no $Os(bpy)_3^{2+}$ is ejected from the coating.

In Fig. 7 are shown the results of triple potential-step experiments with the ring-disk electrode for both unhydrated and hydrated coatings. The potential of the disk electrode was stepped twice between 0.2 and 1.2 V as depicted at the bottom of Fig. 7A. The anodic disk current-time response during the first potential step (Fig. 7A) has the same unusual shape shown in Fig. 6. However, the monotonically decreasing currents obtained during the following two potential steps appear normal. The corresponding ring current responses in Fig. 7B and C show that the anomalous shape of the disk current-time transient in Fig. 7A appears during the period when $Os(bpy)_3^{3+}$ is being ejected from the coating. During the second and third potential steps, there is no significant ejection of $Os(bpy)_3^{3+}$ or $Os(bpy)_3^{2+}$ from the coating, and normal, featureless disk current-time transients are observed.

Repetition of the ring-disk experiments with a fully loaded, hydrated coating produced the responses shown in Fig. 7D, E, and F. $Os(bpy)_3^{3+}$ is ejected from the coating during the first potential step, but the current-time transient has a normal shape, and there is little or no delay between the flow of the anodic disk and cathodic ring currents (Fig. 7D and E). Thus, the unusual shapes of the current transients in Fig. 7A and B are observed only with unhydrated, fully loaded coatings.

Changes in the mass of Nafion coatings during ejection or incorporation of counterions.—A QCM was employed to monitor the changes in mass of Nafion coatings cast on gold film electrodes that had been deposited on the quartz crystal of the QCM.[25,26] Similar experiments have been reported for Nafion coatings that had not been fully loaded with $Os(bpy)_3^{2+}$[16] and, more recently, by Shin *et al.*[15] with fully loaded coatings. As with the results we have already described, the experimental results with the QCM were affected strongly by the procedure used to prepare the Nafion coatings. The solid curve in Fig. 8A shows the first-scan voltammogram for a hydrated Nafion coating on the QCM that was fully loaded with $Os(bpy)_3^{2+}$, and the dotted curve is the steady-state response for the same coating. In Fig. 8B

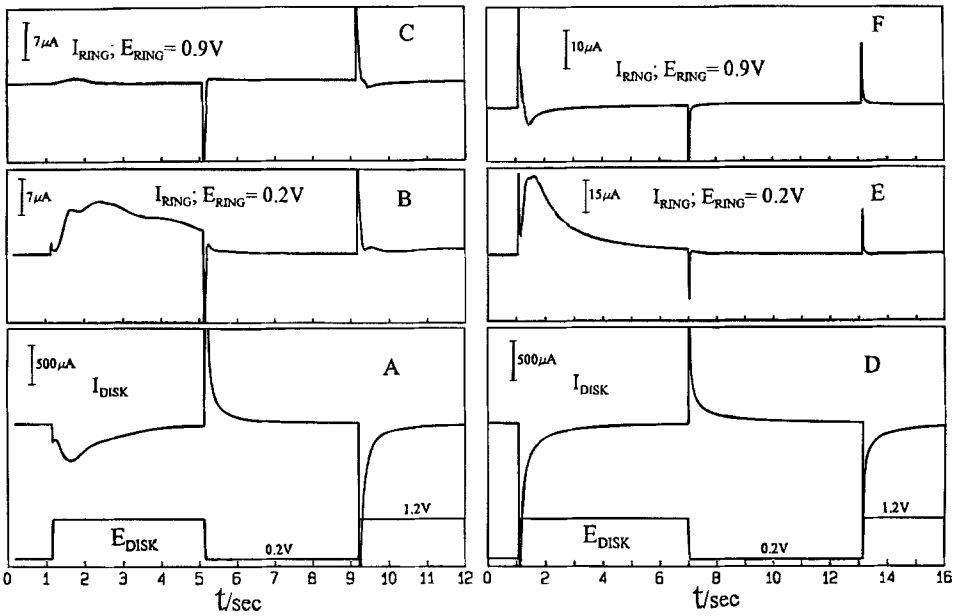

Fig. 7. Current-time transients during multiple potential steps with the rotated ring-coated disk electrode of Fig. 6. The potentials applied to the coated disk electrode are shown at the bottom of the figures. (A) Disk and (B, C) ring current-transients with an unhydrated coating. (D) Disk and (E, F) ring current-transients with a hydrated coating. Other conditions as in Fig. 6.

are shown the corresponding frequency-potential curves that were recorded with the QCM while the cyclic voltammograms in Fig. 8A were being recorded. The increase in the oscillation frequency of the coated quartz crystal during the first oxidative scan indicates a net decrease in mass as is anticipated because of the ejection of $Os(bpy)_3^{3+}$ from the saturated coating during the first oxidative scan (Fig. 5 and 7). The coating regains a portion of the lost mass during the subsequent reductive scan as hydrated cations from the supporting electrolyte (Li^+) are incorporated into the coating. After several voltammetric cycles the coating attains its steady-state condition, and the mass lost during each oxidative scan is regained quantitatively during the subsequent reductive scans (Fig. 8B, dotted curves). The mass difference between the fully oxidized and fully reduced coating at steady state corresponds approximately to the mass of one lithium cation plus seven water molecules per electron, as measured by the coulombic area defined by the cathodic half of the voltammogram. The same type of steady-state behavior has been described recently by Tjärnhage and Sharp,[16] although they observed a greater mass difference that was attributed to the transfer of larger numbers of H_2O molecules with each Li^+ cation. The mass decrease measured during the first oxidative scan in Fig. 8A and B was compared with the calculated mass change that results if electroneutrality within the coating is maintained exclusively by the ejection of $Os(bpy)_3^{3+}$ cations. The quantity of $Os(bpy)_3^{3+}$ ejected for this case was evaluated from the coulombic area, Q_c, defined by the cathodic half of the steady-state voltammogram in Fig. 8A. The results are summarized in the first entry in Table IV. The measured decrease in mass is *ca.* 30% smaller than the mass of the ejected $Os(bpy)_3^{3+/2+}$ counterions, which indicates that additional water is incorporated by the hydrated coating at the same time that the counterion ejection proceeds.

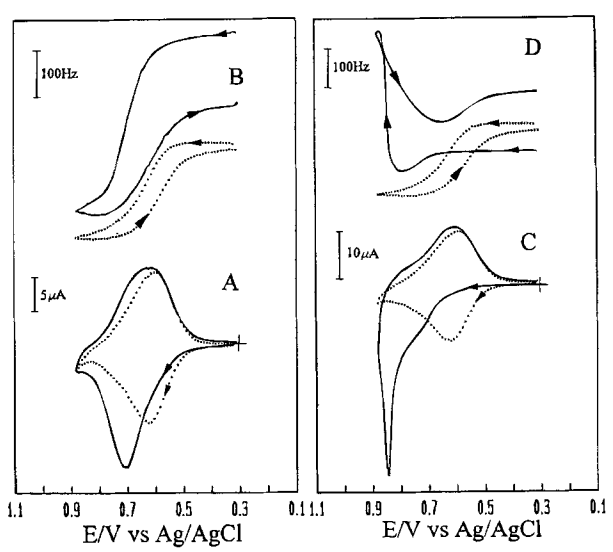

Fig. 8. Mass changes of Nafion coatings fully loaded with $Os(bpy)_3^{2+}$ during cyclic voltammetric scans. (A) Hydrated coating. Solid curve: first-scan voltammogram; dotted curve: steady-state voltammogram obtained after several cycles. Scan rate: 11.6 mV s^{-1}. (B) Corresponding frequency-potential responses recorded with the QCM. The sensitivity of the QCM was 0.9 ng Hz^{-1}, and the ratio of the mass-sensitive area of the QCM gold electrode to its electrochemically active area was 0.9. Increasing frequency (decreasing mass) is plotted downward. (C and D) Repeat of (A) and (B) with an unhydrated coating.

With fully loaded, unhydrated coatings a very different pattern of mass changes occurs. As shown in Fig. 8C and D, the mass of the coating decreases slightly as the anodic current begins to flow near 0.65 V during the first oxidative scan but this small decrease is followed by a sharp increase in mass as the anodic spike of the voltammogram is traversed. The net increase in the mass of the coating (the second entry in Table IV) despite the ejection of a substantial quantity of $Os(bpy)_3^{3+}$ cations from the coating during the first oxidative scan (Table III) indicates that the mass of water molecules incorporated by the unhydrated coating exceeds that of the much heavier $Os(bpy)_3^{3+}$ cations that are ejected. As described above, a small amount of anion incor-

Table IV. Mass changes during the oxidative ejection of $Os(bpy)_3^{2+/3+}$ from Nafion coatings fully loaded with $Os(bpy)_3^{2+}$. [a]

	$Os(bpy)_3^{2+/3+}$ ejected (mol)		Mass changes (μg)	
	$10^{10}\,\Gamma$ [b]	$10^{10}\,\Gamma$ [c]	$(\Delta m)_{calc}$ [d]	$(\Delta m)_{obs}$ [e]
Hydrated coating	8.5	7.7	−0.51	−0.35
Unhydrated coating	8.5	7.7	−0.51	+0.31

[a] Coatings were spin-coated onto the gold-covered surface of a QCM. The quantity of Nafion sulfonate groups in the coatings was determined as in Table III to be 5.1×10^{-9} mol.
[b] The quantity of ejected $Os(bpy)_3^{3+/2+}$ as calculated from $Q_c/2F$ where Q_c is the coulombic area defined by the cathodic half of steady-state voltammograms such as those in Fig. 8A and F is Faraday's constant.
[c] The quantity of $Os(bpy)_3^{3+/2+}$ ejected from the portion of the coating sensed by the QCM (91% of the total area).
[d] Mass of 7.7×10^{-10} mol of $Os(bpy)_3^{3+/2+}$.
[e] Mass change determined from the change in oscillation frequency of the QCM.

poration appears to accompany the ejection of $Os(bpy)_3^{3+}$ from unhydrated coatings, but the latter process is the primary mechanism by which electroneutrality is maintained within the coatings. If anion incorporation is neglected, one calculates that 4.5×10^{-8} mol of H_2O was incorporated by the coating in Fig. 8D to produce the observed mass increase at the end of the oxidative scan despite the ejection of 7.7×10^{-10} mol of $Os(bpy)_3^{3+}$ from the coating. This estimate of the quantity of H_2O entering the coating may be too large because, to avoid the oxidation of the gold electrode, the scan direction was reversed at a potential slightly before the oxidation of the $Os(bpy)_3^{2+}$ in the coating was completed. However, that a net increase in the mass of the coating occurs as $Os(bpy)_3^{3+}$ is ejected from it is clearly established by the behavior shown in Fig. 8C and D.

The response obtained from the QCM during the reductive scan in Fig. 8D is probably the result of a combination of processes. The decrease in mass that occurs immediately after the reversal of the scan direction may reflect loss of water from the coating induced by reincorporation of some $Os(bpy)_3^{2+}$ into the coating as the $Os(bpy)_3^{3+}$ ejected during the oxidative scan is reduced at the coating/solution interface. The increase in mass during the last half of the reductive scan may signal the point at which incorporation of hydrated Li^+ cations became the dominant process affecting the mass of the coating. After several cycles, when the coating attains a steady-state composition, both the voltammetric and QCM responses resemble those for the hydrated coating in Fig. 8A and B.

Close inspection of the solid curves in Fig. 8C and D shows that the anodic oxidation current begins to flow before substantial changes in mass occur with the unhydrated coatings. The inherent response time of the QCM, evaluated in separate experiments in which Ag was electrodeposited on the gold electrode, was *ca.* 0.2 s. This time is much shorter than the observed delay in Fig. 8C and D. We tentatively ascribe the delay to the initial predominance of acetate anion incorporation instead of $Os(bpy)_3^{3+}$ ejection as the charge balancing process. The much smaller molar mass of acetate anions (Mw = 59) compared with $Os(bpy)_3^{3+}$ cations (Mw = 658) means that much smaller mass changes would be detected by the QCM until the ejection of $Os(bpy)_3^{3+}$ from the coatings (accompanied by substantial incorporation of water) became the predominant charge-balancing process.

Discussion

The important influence that the state of hydration of Nafion coatings and membranes can have on their resistances and on their ion-exchange and voltammetric behaviors has been emphasized in various previous reports.[27-38] The present study extends the experimental observations to the special case in which all the counterions in Nafion coatings are replaced by a strongly incorporated, oxidizable cation ($Os(bpy)_3^{2+}$). With such fully loaded coatings, the effects of differing extents of hydration of the coatings become particularly apparent.

The extent of hydration of Nafion coatings is affected by several factors including the water content of the solvent from which the coatings are cast,[36] the humidity of the atmosphere in which the freshly deposited coatings are dried,[35,38] and the treatments (soaked or not soaked in aqueous solutions) to which the freshly prepared coatings are subjected.[33] In the present study the first two factors, which have been previously explored, were maintained constant to focus primarily on the effects of presoaking freshly cast coatings in aqueous media. The first-scan voltammograms in Fig. 1 and 2 clearly demonstrate the differences between the behavior of presoaked (hydrated) and unsoaked (unhydrated) coatings. The unhydrated, fully loaded coatings require much more positive potentials for the oxidation of $Os(bpy)_3^{2+}$ to commence (Fig. 1A). Charge propagation across Nafion coatings in which reversible redox couples have been incorporated is recognized to occur in general by both physical motion of the counterions and electron-hopping between more or less immobile pairs of the oxidized and reduced counterions.[3,6,13,39-42] However, in coatings fully loaded with $Os(bpy)_3^{2+}$, substantial physical motion of the counterions must occur during their oxidation so that some of them can be ejected from the coating to maintain electroneutrality. We attribute the larger potentials required to initiate the oxidation of $Os(bpy)_3^{2+}$ within coatings that have not been soaked in water before loading with $Os(bpy)_3^{2+}$ to the dehydrated state of these coatings. Immediate loading of freshly cast coatings from 1 m*M* solutions of $Os(bpy)_3^{2+}$ diminishes the extent of hydration of the coatings because the sulfonate groups of the Nafion which are solvated by water molecules when the coatings contain alkali cations or protons as counterions,[29,31,43] are consumed instead in the formation of tight ion pairs with the incorporated $Os(bpy)_3^{2+}$ counterions.[29,31,44] Any sulfonate groups which may become partially hydrated initially are eventually dehydrated during the 12 to 24 h required to obtain full loading of coatings that are not presoaked in water. Fully loaded coatings of this type may be regarded as deposits of "Nafionate" salts of $Os(bpy)_3^{2+}$. As pointed out by Sharp *et al.*,[13] the volume of such fully loaded Nafion coatings is not much larger than the calculated volume of the $Os(bpy)_3^{2+}$ cations that they contain as measured coulometrically. Thus, it is not surprising that these coatings contain little water. Their resistances are high because ionic motion is restricted in the dehydrated, saltlike environment, and higher voltages are required to initiate current flow as reflected in the more positive anodic peak potentials during first oxidative scans (Fig. 1A). The spiked shape of the anodic current response may be the result of a kind of positive feedback: the counterion ejection that accompanies the anodic oxidation provides more space to accommodate movement of the remaining counterions. In addition, water molecules (and, apparently, some anions) enter the coating to occupy some or all the space vacated by the ejected cations. The resulting increase in hydration and the presence of mobile anions diminishes the resistance of the coating. As a result, the flow of current increases, and the process becomes self-enhancing. During the reductive half of the first voltammetric cycle unipositive, hydrophilic Li^+ cations are incorporated into the coating, which remains largely hydrated and additional cycles yield the normally shaped, steady-state responses of coatings where most of the ionic current is carried by the motion of the alkali cation (Fig. 1, dotted curves). The key factor required to obtain responses like that in Fig. 1A is the essentially complete replacement of alkali (or proton) counterions with hydrophobic, electrostatically cross-linking $Os(bpy)_3^{2+}$ (or similar) counterions that produce dehydrated coatings. The reason that responses like that in Fig. 1A have not been previously described (except in Ref. 14) is probably because of the long loading times (12 to 24 h) required to obtain coatings that are truly fully loaded with the reduced form of the complex and that the anodic spike is only present in first-scan voltammograms. For example, in Ref. 36 it was desired to prepare Nafion coatings fully loaded with $Ru(bpy)_3^{2+}$. The level of loading was assessed from the peak currents of cyclic voltammograms recorded after various loading times. When these peak currents stopped increasing, the Nafion was taken to be saturated. However, this method of monitoring the loading is most likely to produce coatings saturated with respect to $Ru(bpy)_3^{3+}$ instead of $Ru(bpy)_3^{2+}$, and thus no anodic spike in the voltammetric response is expected, and none was observed. When Nafion coatings are fully loaded with $Ru(bpy)_3^{2+}$ using the extended loading times employed, first-scan voltammograms that resemble that in Fig. 1A can be obtained. An example is shown in Fig. 9.

The rotating ring-disk experiments with fully loaded films (Fig. 5) showed a delay between the initiation of the oxidation of $Os(bpy)_3^{2+}$ and the ejection of $Os(bpy)_3^{3+}$ (or $Os(bpy)_3^{2+}$) from the Nafion coatings. The delayed ejection may arise in two ways: the $Os(bpy)_3^{2+}$ counterions in the outermost portion of the coating may be partially replaced by Li^+ cations of the supporting electrolyte before the rotat-

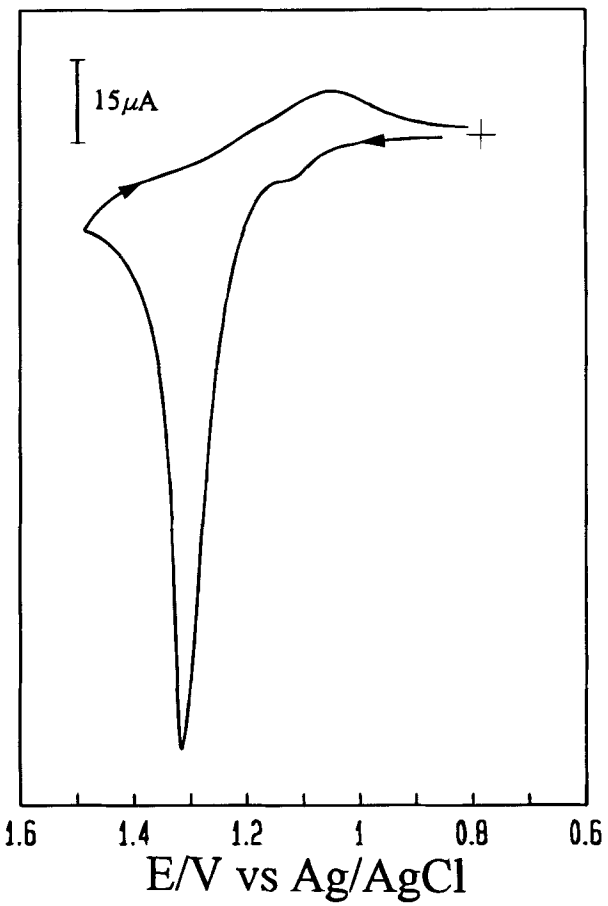

Fig. 9. First-scan cyclic voltammogram for an unhydrated Nafion coating fully loaded with $Ru(bpy)_3^{2+}$. Other conditions as in Fig. 1.

ing disk experiments are begun. These more mobile Li^+ cations may then carry the cationic ejection current during the early stages of the oxidation of the $Os(bpy)_3^{2+}$ cation that are retained in the interior of the coating. A second possibility is that anion incorporation instead of cation ejection carries the initial ionic current across the coating/solution interface. We take the presence of a small cathodic wave at potentials more positive than that of the primary cathodic peak in the first scan voltammograms for fully loaded, unhydrated coatings (Fig. 1A and 4) as evidence for the presence of incorporated anions despite the usually high cation permselectivity of Nafion coatings. The apparent diminishment of this permselectivity in fully loaded, unhydrated coatings (Table I) may be the result of the formation of such tight ion pairs between the $Os(bpy)_3^{3+/2+}$ counterions and the Nafion sulfonate groups that the electrostatic Donnan potential created by the fixed anionic sites is substantially diminished. The apparent absence of anion incorporation into hydrated coatings (Fig. 1B, Table I) may then be understood in terms of less tight ion pairing in Nafion coatings that have been allowed to hydrate before being fully loaded with $Os(bpy)_3^{2+}$.

Nafion coatings that are allowed to soak in water or aqueous buffer solutions before they are loaded to saturation with $Os(bpy)_3^{2+}$ incorporate essentially the same quantities of the cation as unhydrated coatings but exhibit first-scan voltammograms without the sharp spike (Fig. 1B). The presoaking procedure evidently produces a hydrated coating with a structure that is different from that of unsoaked coatings. When the Nafion sulfonate groups are allowed to become fully hydrated before exposure to $Os(bpy)_3^{2+}$, the coating retains much of its water during the incorporation of the $Os(bpy)_3^{2+}$, which also proceeds much more rapidly than with unhydrated coatings. The inference, also suggested in earlier studies,[34,45] is that the ports and channels in the Nafion[46,47] are filled with water which facilitates ionic motion and decreases the coating resistance. $Os(bpy)_3^{2+}$ cations are ejected from fully loaded and hydrated as well as unhydrated coatings, but the accompanying incorporation of water into the coating is much greater with unhydrated coatings (Table IV) showing that the fully loaded coatings prepared by the two procedures retain substantially different internal structures, even when fully loaded with $Os(bpy)_3^{2+}$. Such long-lived structural differences among Nafion coatings and membranes containing differing amounts of water have been observed in previous investigations.[33,48,49]

Consequences of the ejection of $Os(bpy)_3^{2+}$ from fully loaded coatings.—The rotating ring-disk electrode experiments clearly demonstrated the ejection of substantial quantities of $Os(bpy)_3^{3+}$ from both hydrated and unhydrated, fully loaded coatings (Fig. 5). A small quantity of $Os(bpy)_3^{2+}$ was initially ejected from hydrated coatings (Fig. 5B and 7F), but the predominant process involved in the maintenance of electroneutrality within the coatings was the ejection of $Os(bpy)_3^{3+}$.

In a previous study it was suggested that the higher electric fields necessary to produce current flow through fully loaded coatings caused the more highly charged counterion to be preferentially accelerated and ejected. This notion remains the most likely possibility, although it is puzzling that $Os(bpy)_3^{2+}$ cations, which are the only cations initially present at the coating/solution interface with fully loaded coatings, are not ejected as the $Os(bpy)_3^{2+}$ cations initially present at the electrode/coating interface are electro-oxidized. The diminished permselectivity of fully loaded coatings (Table I) and the voltammetric evidence that anions may be incorporated in them (Fig. 4) suggest that anion incorporation may be substantial during the early stages of the electro-oxidation of fully loaded, unhydrated coatings. However, once sufficient $Os(bpy)_3^{3+}$ appears at the coating/solution interface, the ejection of the tripositive cation into the solution becomes the dominating process for the flow of ionic current at this interface. Values as large as 5×10^{-9} cm^2 s^{-1} have been reported for the apparent diffusion coefficient of $Os(bpy)_3^{3+/2+}$ cations in highly loaded Nafion coatings.[40] Thus, for the coating thicknesses employed here, *ca.* 3.4×10^{-5} cm, one calculates that about 0.1 s is required for $Os(bpy)_3^{3+}$ to diffuse across the coatings. Apparent diffusion coefficients in coatings fully loaded with $Os(bpy)_3^{2+}$ have not been reported because of the severely non-Cottrellian behavior that is present during the first oxidative potential step (Fig. 6). However, the electric fields present in coatings that are highly loaded but contain fewer than one $Os(bpy)_3^{2+}$ cation per three SO_3^- sites, are known to enhance the effective rate of diffusion of $Os(bpy)_3^{2+}$ counterions substantially.[41] At least one-third of the counterions in such coatings are mobile, electroinactive cations,[41] and the enhancement in the diffusion coefficient of the $Os(bpy)_3^{3+/2+}$ cations should only increase as the quantity of mobile electroinactive counterions is decreased toward zero.[41] Thus, if the kinetic barrier opposing the ejection of $Os(bpy)_3^{2+}$ from coatings resulted in an ejection rate that was slower than the rate of appearance of $Os(bpy)_3^{3+}$ at the coating/solution interface (perhaps accompanied by some anion incorporation into the coating), it does not seem unreasonable that the same electric field responsible for the acceleration of the diffusion of $Os(bpy)_3^{3+/2+}$ counterions may act to cause the more highly charged counterion to be preferentially ejected from the coating.

The space inside coatings that was occupied by the ejected cations is presumably taken up by incorporated water molecules and expansions of portions of the polyelectrolyte chains. Not all the vacated space in hydrated coatings can be occupied by incorporated H_2O molecules because the density of H_2O molecules exceeds that of the relatively voluminous $Os(bpy)_3^{3+}$ cations, and a net decrease in mass is observed during ejection of $Os(bpy)_3^{3+}$ from hydrated coatings. A possible explanation is that hydrophobic $Os(bpy)_3^{3+/2+}$ cations occupy hydrophobic portions of the Nafion coatings that are not accessible to H_2O molecules. Following ejection of the hydrophobic counterion, these

portions of the coatings may remain empty or be occupied by expansion of portions of the fluorocarbon backbone of the Nafion chains.

The gain in mass that is observed as $Os(bpy)_3^{3+}$ cations are ejected from unhydrated, fully loaded Nafion coatings probably reflects the entry of H_2O molecules into hydrophilic portions of the coatings that remained blocked by the presence of $Os(bpy)_3^{2+}$ cations in the entry channels of the unhydrated, fully loaded coatings. Because of the simultaneous entry of unknown quantities of H_2O molecules and the exit of $Os(bpy)_3^{3+}$ counterions from the coatings, the net mass changes observed did not provide an independent measure of the quantities of $Os(bpy)_3^{3+}$ ejected. However, the data summarized in Table IV imply that about 60 water molecules are incorporated by unhydrated coatings for every $Os(bpy)_3^{3+}$ cation that is ejected from them. This values is only approximate because changes in the viscoelasticity of the coating during cation ejection and water incorporation were neglected on the basis of the recent report by Tjärnhage and Sharp[16] that such changes did not invalidate QCM measurements with Nafion coatings loaded with $Os(bpy)_3^{2+}$ below saturation levels. In any case, it is striking that the volume of an $Os(bpy)_3^{3+}$ cation calculated from a radius of 7 Å[50] is *ca.* 1.4×10^3 Å^3 and the volume of 60 water molecules is 1.8×10^3 Å^3.[51] Thus, the volume vacated by each ejected $Os(bpy)_3^{3+}$ cation may accommodate about 80% of the estimated number of water molecules that are incorporated by the coating as each $Os(bpy)_3^{3+}$ cation is ejected.

Conclusions

The results of this study support and supplement previous reports that describe the effects of hydration on the properties of Nafion. The new results obtained with coatings fully loaded with $Os(bpy)_3^{2+}$ but containing rather little water indicate that such coatings take on the properties of a Nafionate salt. These properties include low ionic and electronic conductance and a high affinity for water that is expressed only when a portion of the $Os(bpy)_3^{2+}$ counterions are oxidatively ejected from the coatings to provide the space for water molecules to enter the coatings. The dynamics of the counterion ejection and accompanying water and (apparently) anion incorporation by the coatings can be observed by transient rotating ring-disk voltammetry and quartz crystal microgravimetry. High electric fields are present during forced current flow through fully loaded, unhydrated coatings before they are cycled to attain a steady-state composition that includes both mobile alkali cations and much less mobile $Os(bpy)_3^{3+/2+}$ counterions. These electric fields play an important role in the counterion ejection process and on chemical reactions carried out within the coatings. Studies of the latter effects are the subject of continuing studies.

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